Co-Optimization of
Fuels & Engines

Fuel Property Characterization and Prediction

Presenter, Gina Fioroni

G.M Fioroni, M. Rahimi, R. Grout, S. Kim, and R.L. McCormick (NREL)
T. Bays (PNNL)
W. Pitz, S. Wagnon (LLNL)

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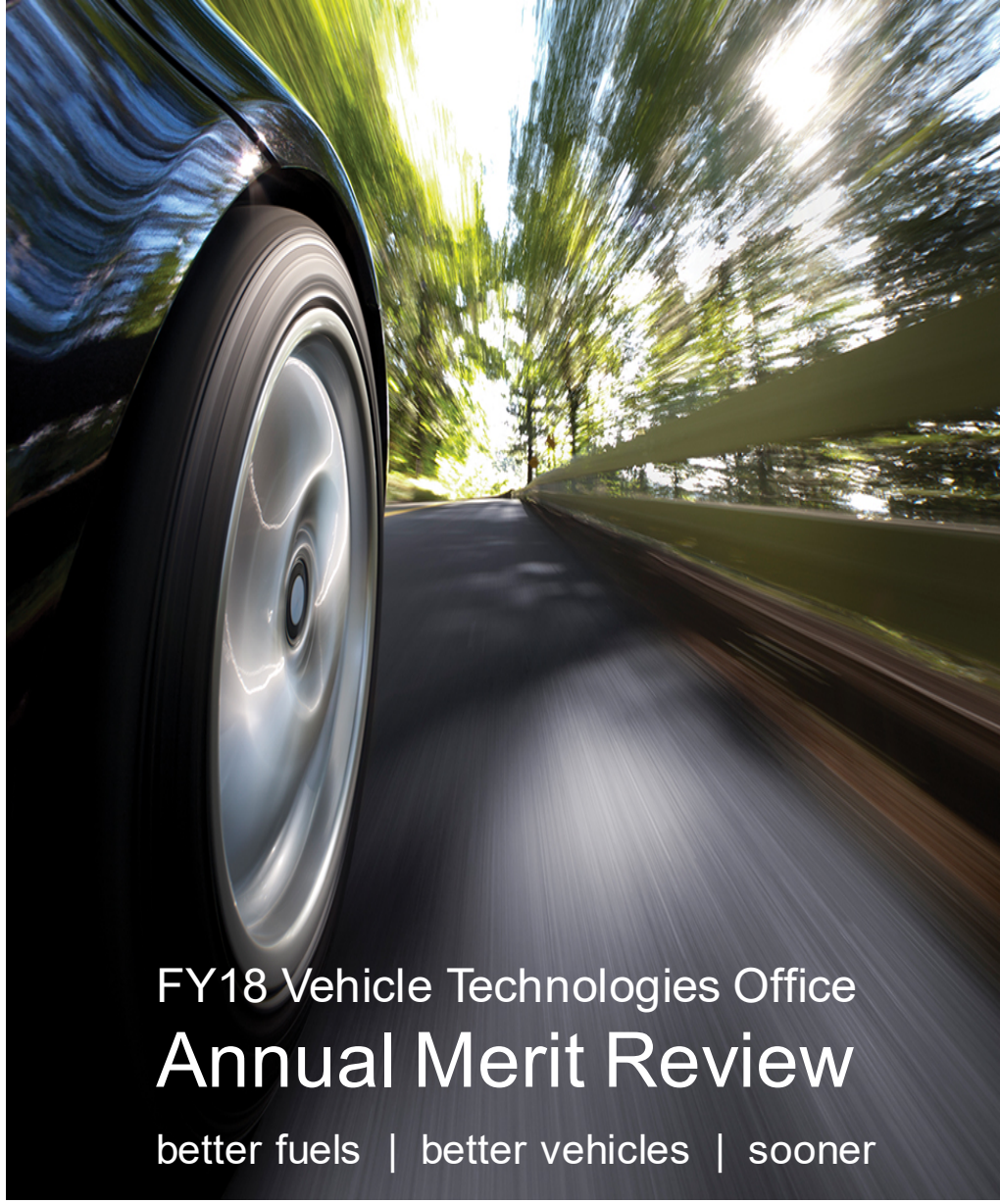
Project # FT051



FY18 Vehicle Technologies Office
Annual Merit Review
better fuels | better vehicles | sooner

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Overview

Timeline

- Project start date: 10/1/2015
- Project end date: *9/30/2018
- Percent complete: 88%

Budget

Task	FY16	FY17	FY18
F.1.2.2: PNNL Fuel Property Blending Model	$0	$150K	$125K
F.1.2.3: LLNL Fuel Property Blending Model	$75K	$75K	$65K
F.1.3.2: NREL Heat of Vaporization Measurement for Full Boiling Range Fuels	$200K	$200K	($200K requested)
F.2.1.4: NREL Flow Reactor Autoignition Kinetic Mechanism Development and Validation	$150K	$0	$90K + ($60k requested)

*Start and end dates refer to three-year life cycle of DOE lab-call projects. Co-Optima is expected to extend past the end of FY18.

Barriers

- Fuel evaporation phenomena that impact autoignition, mixing, and pollutant formation are poorly understood
- Improved models of autoignition mechanisms, kinetics, and blending effects are needed for all combustion modes
- Lack of data and models on mechanisms of soot formation hinder our ability to design fuels with low sooting tendency

Partners

- Partners include nine national labs, 13 universities, an external advisory board, and stakeholders (145 individuals from 86 organizations)

Relevance

Impact

- Research into better integration of fuels and engines is critical to accelerating progress towards our economic development, energy security, and emissions goals

Objectives

- Improved measurement (or prediction) of critical fuel properties relevant to engine efficiency
  - Gasoline volatility and evaporation
  - Autoignition mechanism and kinetics including RON and MON prediction
  - PM formation and precursor formation mechanisms
- Reveal underlying physical chemistry
- LDSI focus in 2017/2018
- Transition to multimode, MD/HD diesel, and advanced CI combustion in FY19

CI: compression ignition
HD: heavy duty
LDSI: light-duty spark ignition
MD: medium duty
MON: motor octane number
PM: particulate matter
RON: research octane number

Milestones

Month/Year	Description of Milestone or Go/No-Go Decision	Status	Lab
September 2018	Draft article on impact of alcohol affects on HOV	On Target	NREL
June 2018	Report or draft article comparing experimental results to simulation for LDSI most promising blendstocks (flow reactor autoignition)	On Target	NREL
March 2018	Predict effect of 2-3 different BOBs with the same AKI (or RON) on the blending behavior of Co-Optima downselected compounds in terms of RON and OS	Completed	LLNL
December 2018	Report detailing inputs to the fuel property blending model to predict DCN built from five binary blends of two components and liquid-solidification results for four fuel surrogates containing combinations of a total of 13 components, including measuring the effect of eight fuel additives in one surrogate	On Target	PNNL
September 2018	Report detailing trends in oxygenate clustering for one alcohol in SI/MCCI/ACI fuels, and high-pressure solid-liquid phase behavior of 8 Co-Optima blendstocks in BOBs	On Target	PNNL

ACI: advanced compression ignition
AKI: anti-knock index
BOB: blendstock for oxygenate blending
DCN: derived cetane number
HOV: heat of vaporization
MCCI: mixing-controlled CI combustion
OS: octane sensitivity
SI: spark ignition
LLNL: Lawrence Livermore National Laboratory
NREL: National Renewable Energy Laboratory
PNNL: Pacific Northwest National Laboratory

Approach

Measurement and understanding of gasoline-like fuel volatility

- F.1.2.2 Apply nuclear magnetic resonance (NMR) diffusion measurements to reveal clustering of alcohol molecules and the impact of this phenomenon on non-ideal solution behavior (Reid vapor pressure [RVP]) – *PNNL*
- F.1.3.2 Utilize simultaneous differential scanning calorimetry (DSC)/ thermogravimetric analysis (TGA) instrument coupled to a mass spectrometer, and detailed analysis, to quantify and understand heat of vaporization effects on gasoline evaporation – *NREL*

Autoignition metrics and mechanisms

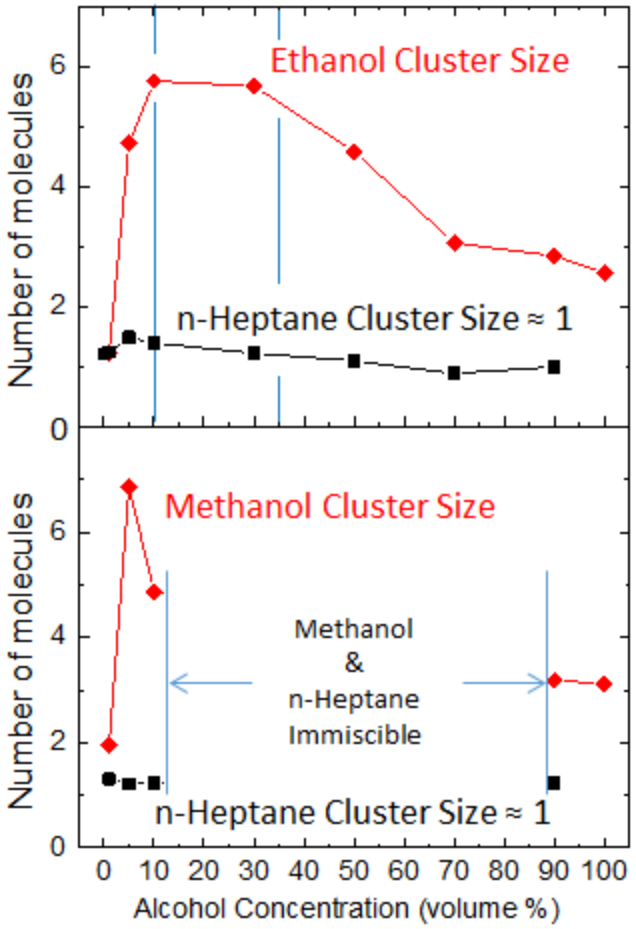
- F.1.2.3 Prediction of RON and OS of blends from kinetic simulations - *LLNL*
- F.2.1.4 Flow reactor study to predict RON and OS, as well as reveal autoignition and PM formation precursor mechanisms - *NREL*

PNNL (Bays): Fuel Property Blending Model: The Impact of Oxygenate Clustering on Fuel Properties

Accomplishment

Determine if solution structure imparted by oxygenates impacts RVP

Number of Molecules in the Clusters



Ethanol in n-Heptane

Methanol in n-Heptane

- From the Diffusion Coefficient:
  - Molecular weight determination yields number of molecules in a cluster
  - Stokes-Einstein Equation yields the "hydrodynamic radius" (cluster size)
  - Cluster radius and number of molecules are in agreement
  - Changes in cluster size with increasing alcohol concentration likely result in transitioning between short- and long-range hydrogen bonding
- *Initial Conclusions*: Solution structure arises from:
  - short-range hydrogen bonding, which promotes cluster formation at low alcohol concentrations, and
  - long-range hydrogen bonding at higher alcohol concentrations, which reduces the number of discrete ethanol clusters in favor of contiguous ethanol networks.

Impact: Reveal how solution structure of oxygenates impacts RVP

PNNL (Bays): Fuel Property Blending Model: The Impact of Oxygenate Clustering on Fuel Properties

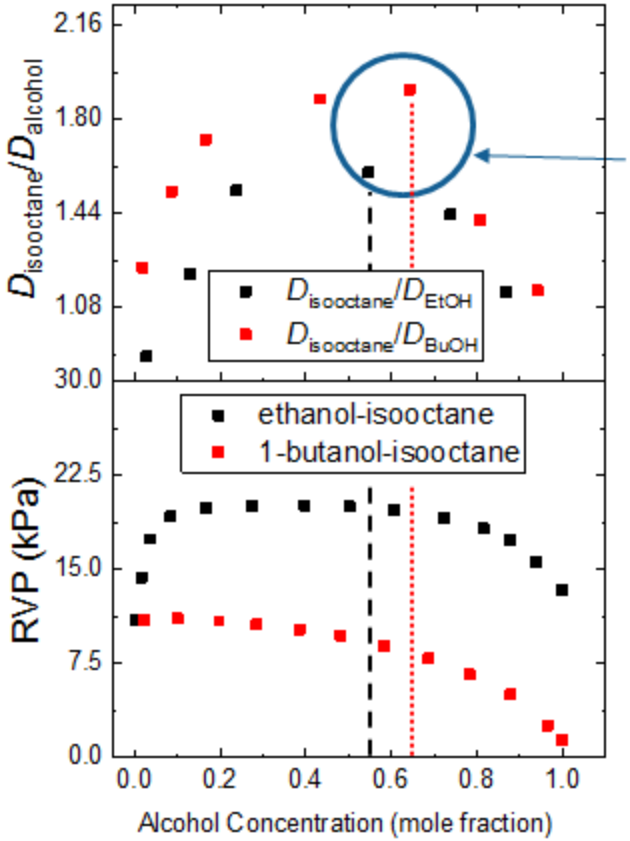
Accomplishment

Determine if solution structure imparted by oxygenates impacts RVP

RVP as a Function of Alcohol Mole Fraction Compared with Alcohol Cluster Size

Relative Alcohol Cluster Size

Reid Vapor Pressure



Where the alcohol diffuses the slowest relative to the solvent (i.e., cluster sizes are the largest)

Ethanol

X=0.55 or ~35% volume

n-Butanol

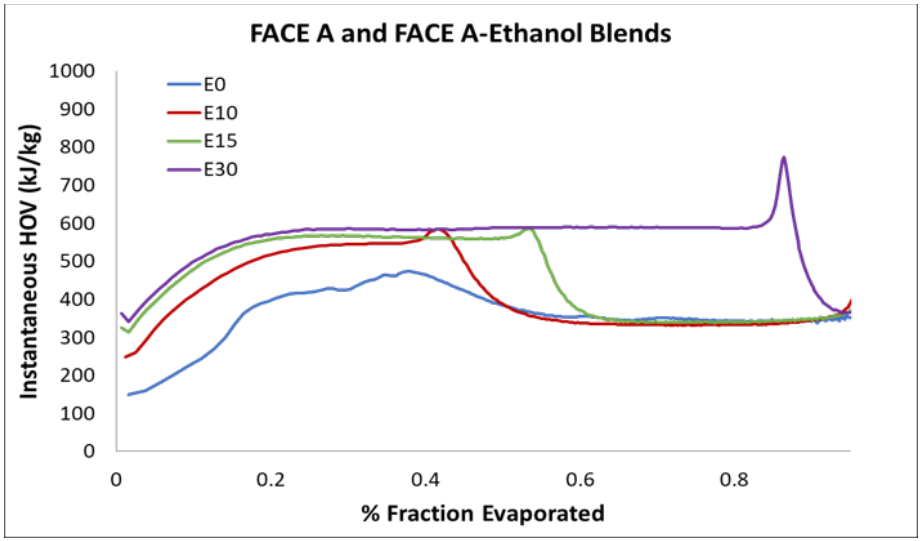
X=0.65 or ~55% volume

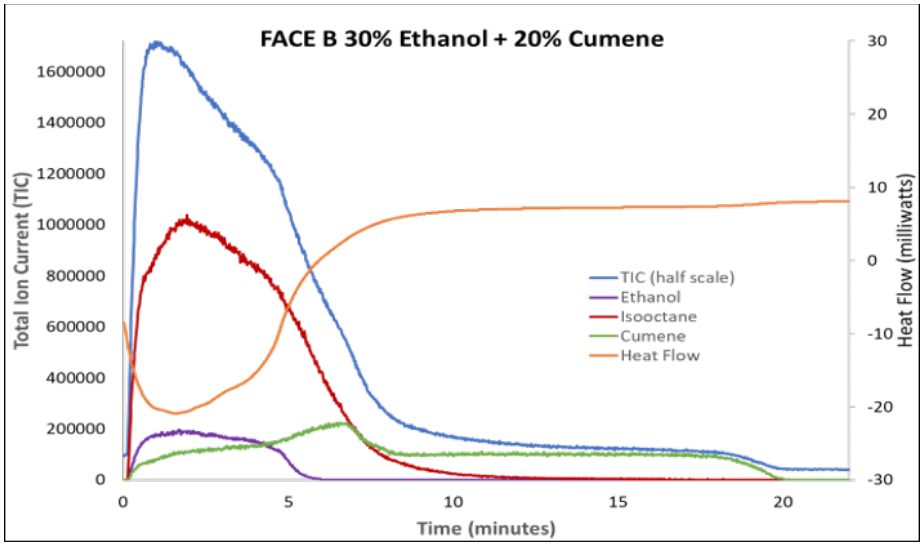
- Amount of long-range hydrogen bonding may be related to RVP
  - Above 35% volume ethanol clusters decrease in size as long-range hydrogen bonding dominates
  - Weaker hydrogen bonding in n-butanol implies that more (55% volume) is required before long-range hydrogen bonding becomes effective
- The immediate decrease in RVP for n-butanol suggests more than cluster size impacts RVP
- ***Conclusion/Impact: Solution structure contributes to RVP, but more information is required to better understand the impact***

NREL (Fioroni/McCormick) Heat of Vaporization Measurement for Full Boiling Range Gasolines

Accomplishment

Apparatus for measuring HOV was coupled to a high-resolution mass spectrometer revealing interactions that impact heat and composition evolution during evaporation



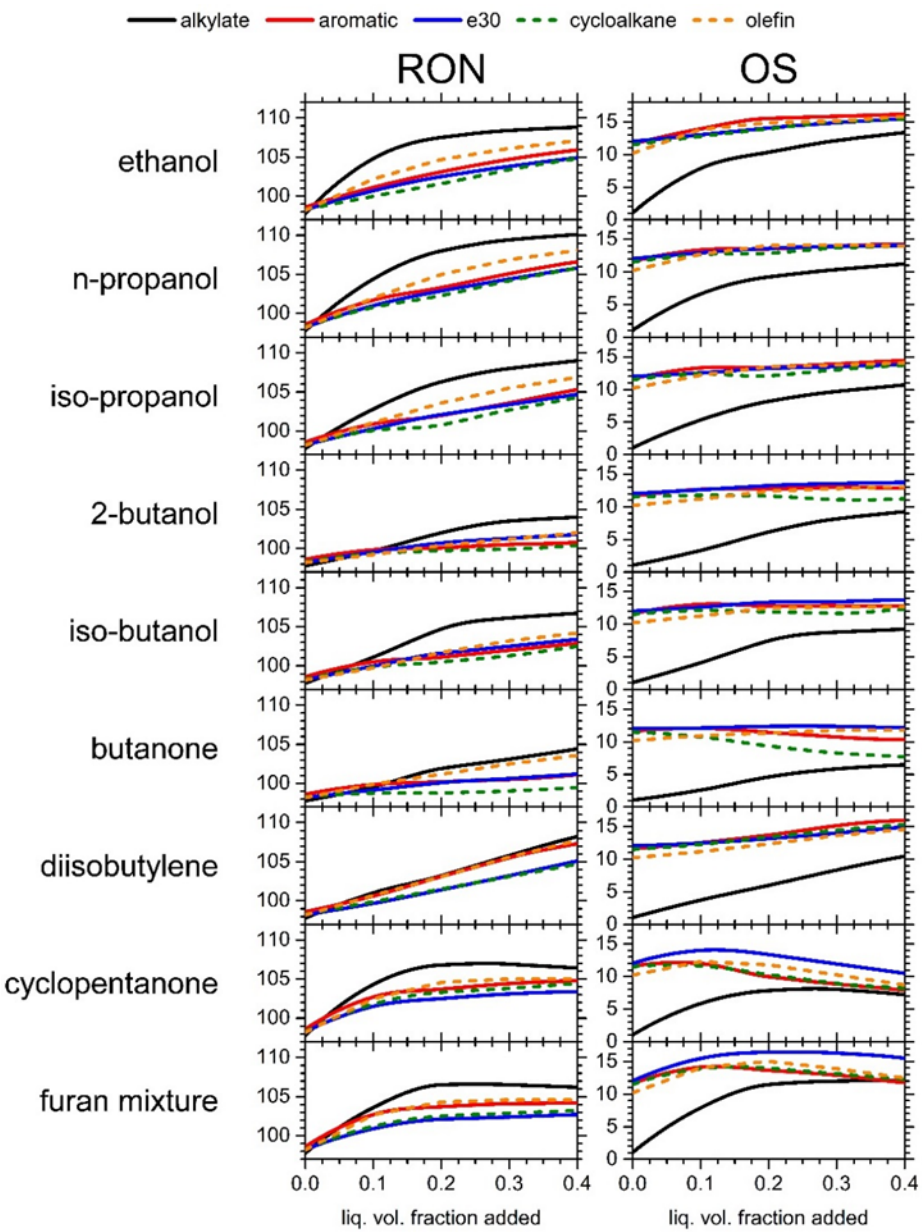


- HOV is a key fuel property for understanding how to increase efficiency for boosted SI engines and affects P-T trajectory in ACI combustion modes
- Measured total HOV of full boiling range gasolines – and the Co-Optima Core gasolines
- "Instantaneous HOV" concept has been further developed
- Coupling DSC/TGA to high-resolution mass spectrometer reveals compound evolution during evaporation process – demonstrates EtOH interaction with aromatic components in fuel
- ***Impact: Fuel evaporation phenomena can impact autoignition, mixing, and pollutant formation***

FACE: Fuels for Advanced Combustion Engines
P-T: pressure-temperature

LLNL (Pitz/Wagnon) Fuel Property Blending Model: Blending of High-Performance Fuels into Co-Optima Core Fuels Enhances Octane Properties

Accomplishment



Kinetic model predictions allow evaluation of different high-performance fuels (HPFs)

Approach:

- Developed fuel-mixture surrogates to represent properties of core fuels
- 5 Co-Optima core fuels have similar RON (~98)
- Co-Optima gasoline + HPFs kinetic model and neural network (Whitesides) used to compute RON and OS for blends

Results:

- Alkylate fuel exhibits the greatest octane (RON and OS) enhancement from addition of HPFs
- Other core fuels are predicted to have similar RON and OS trends

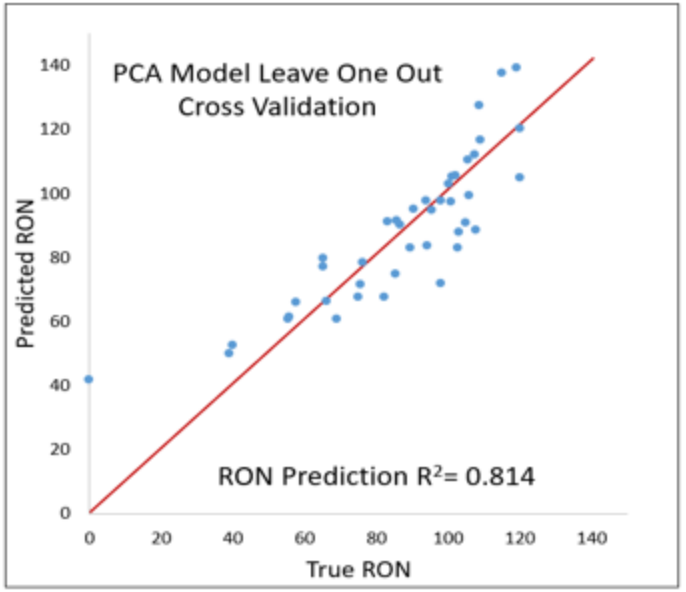
Next steps:

- Ongoing work to understand the kinetic and physical property contributions to the octane blending behavior
- ***Impact: Prediction of fuel properties at engine conditions allows researchers to evaluate advanced combustion strategies***

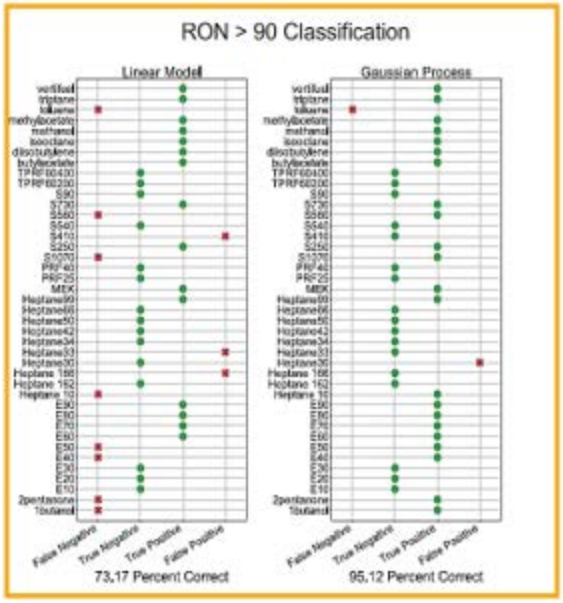
NREL (Fioroni/Grout/McCormick): Flow Reactor Autoignition Kinetic Mechanism Development and Validation *Accomplishment*

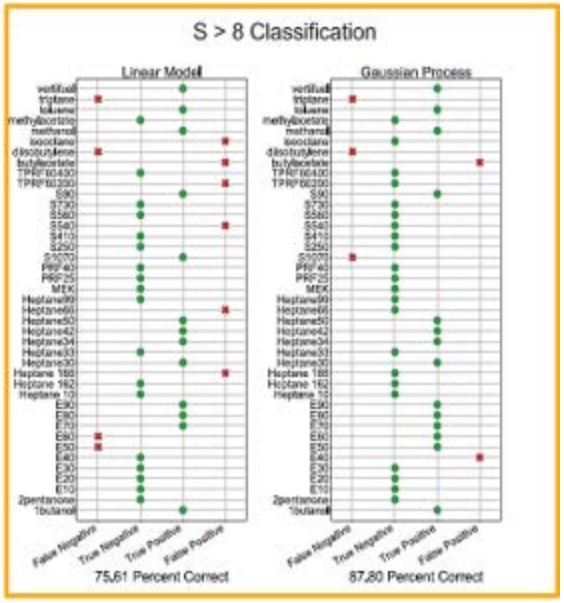
Accurate method to predict compounds having RON (and OS at lower accuracy) over a specified level has been developed

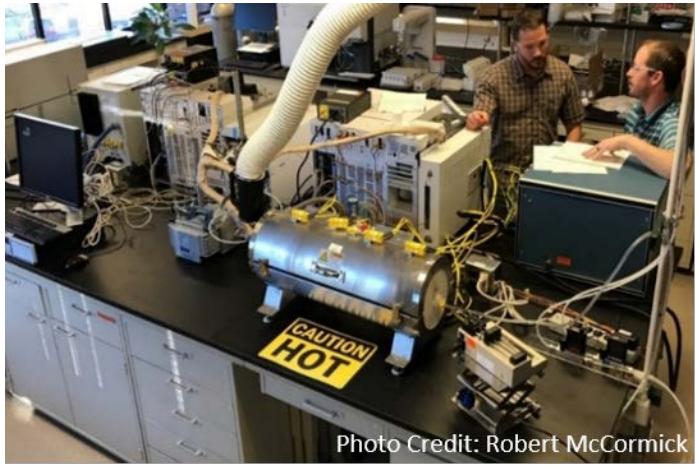
- Last year reported simple data analysis for micro plug flow reactor for prediction of RON and OS
- In the remaining months of FY17 we developed a Gaussian process regression and classification to predict RON and OS
- ***Impact: A method to estimate RON and OS using less than 0.1 mL of a compound– highly valuable for screening proposed new fuels***



Gaussian Process Regression Classification



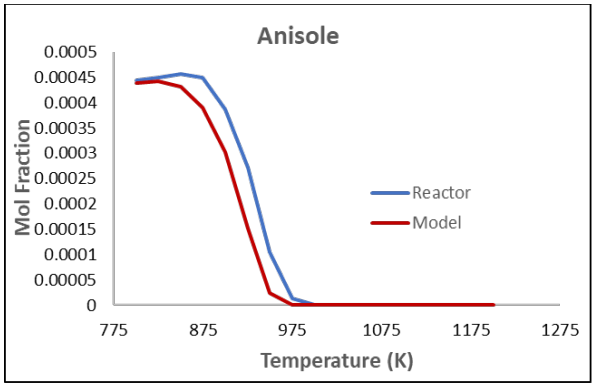


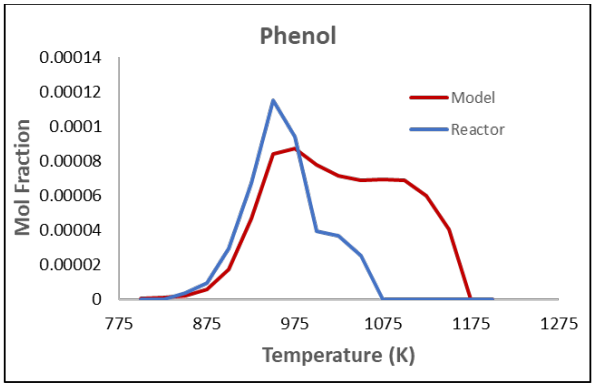


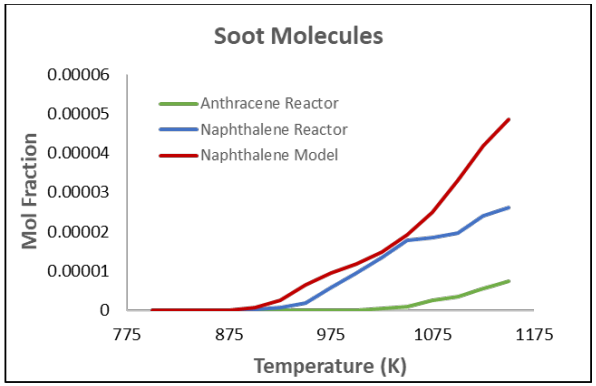
PCA: Principal Component Analysis

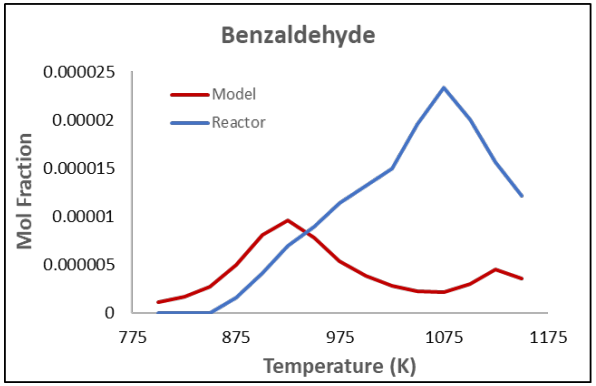
NREL (Fioroni/McCormick): Flow Reactor Autoignition Kinetic Mechanism Development and Validation *Accomplishment*

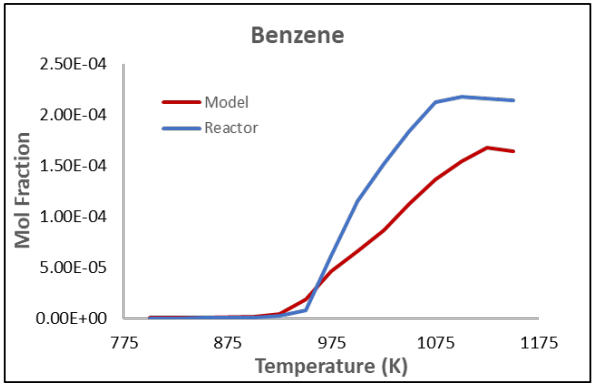
Autoignition of anisole examined as model biofuel and compared with new mechanism developed by LLNL



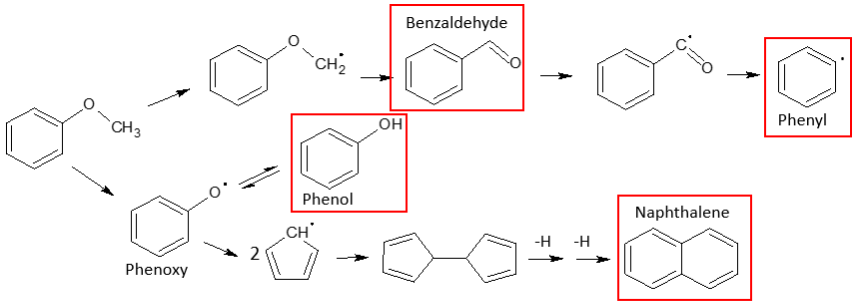








- Demonstrates that key intermediates are not properly predicted by the model and further model development is necessary
- Observed formation of soot precursor molecules

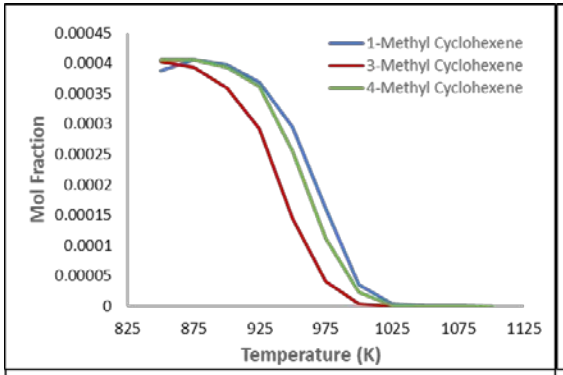


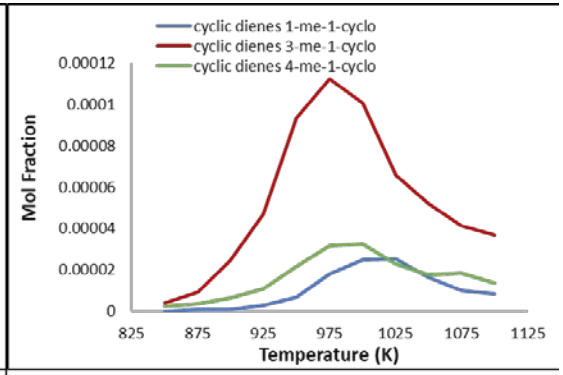
Scheer, A., et al., *J. Phys. Chem. A* **2010**, *114*, 9043-9056

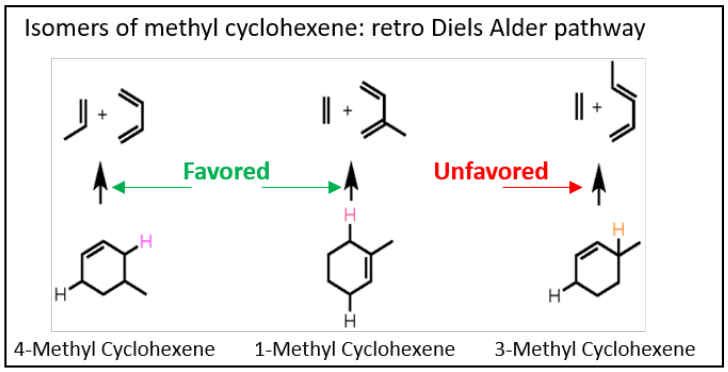
Impact: A simple, yet powerful new tool for revealing autoignition mechanisms and validating kinetic simulations has been developed and can be rapidly applied to a wide range of fuel molecules/blendstocks

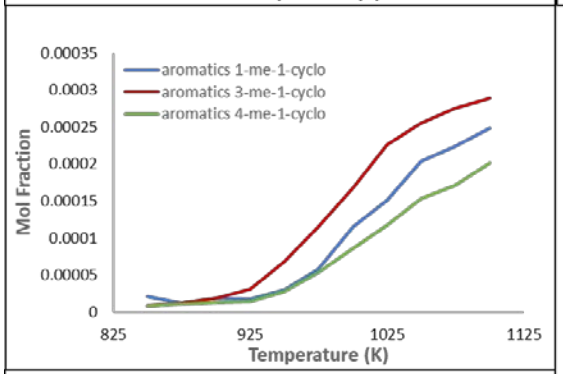
NREL (Fioroni/Kim/McCormick): Flow Reactor Autoignition Kinetic Mechanism Development and Validation *Accomplishment*

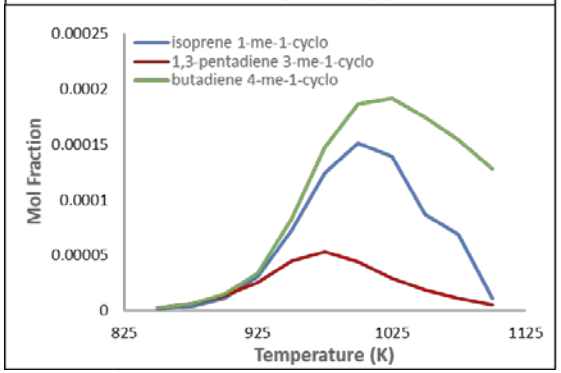
The formation of soot precursors in combustion of isomers of methyl cyclohexene was investigated in flow reactor experiments and through density functional theory simulations











- Yield Sooting Index (YSI) is a useful sooting tendency metric
- A machine learning model over-predicts YSI for two out of three methyl cyclohexene isomers
- QM simulations and flow reactor experiments show low-YSI isomers (1-methyl cyclohexene and 4-methyl cyclohexene) preferentially react via a ring opening pathway
- Higher sooting 3-methyl cyclohexene reacts by dehydrogenation leading more directly to soot precursors
- This points to missing chemistry in the predictive model
- ***Impact: Poor understanding of the mechanisms of soot formation hinder our ability to design fuels with low sooting tendency***

QM: quantum mechanical

Response to Previous Year Reviewers' Comments

"the work to measure the heat of vaporization of multicomponent mixtures characteristic of "real" fuels has a lot of merit. The reviewer added that the development of small volume testers to measure key properties of fuel components that are not available in large enough quantity for conventional analytical devices (such as Cooperative Fuel Research [CFR] engines for octane determination) would be very valuable." *We are grateful that the reviewers recognize the importance of this research.*

"the Merit Function has a term for particulate matter index (PMI), but lacks terms for other important emissions components. The reviewer added that this leads to confusion as to whether the Merit Function is solely focused on efficiency, or if it also tries to account for some, but not all emissions." *PMI is included in a term that tries to quantify the engine efficiency impact of a gasoline particle filter, so the Merit Function is solely focused on efficiency.*

"The reviewer added that there is important research going on in this project that needs to continue. The reviewer did not see flame speed (SL) or PMI in the dataset, and commented that it was part of the merit function." *Efforts to measure and improve PMI are discussed in the Emissions, Emission Control, and Sprays presentation. Flame speed was determined to be of minor importance for stoichiometric boosted SI but of critical importance for dilute SI and beyond MON, ACI conditions. Co-Optima does not currently have a project measuring turbulent flame speed, however, there is an effort at University of Central Florida (UCF) to measure laminar flame speed. Also, LLNL is computing flame speeds with kinetic models and validating them by comparison to data from UCF, Lund University, and literature.*

Collaboration and Coordination with Other Institutions

- **Collaboration of nine national laboratories**
- **University of Connecticut** (*Kinetic Simulations*)
- **Yale University** (*YSI Measurements*)
- **Colorado State University** (*Advanced Distillation and Droplet Evaporation Simulations*)
- **Coordinating Research Council** (*HOV Measurements-AVFL-27, Diesel Surrogate Work-AVFL-18a*)
- **Pennsylvania State University** (*YSI Predictions of Soot Using Co-Optima HPFs Fuel Kinetic Models)*
- **General Motors** (*HOV Measurements and Effects in Engine – SAE 2018-01-0358*)
- **Ford Motor Company** (*HOV Measurements in CRC AVFL-27*)
- **Massachusetts Institute of Technology** *(Rate Constant Calculations of Key Low Temperature Reactions for Kinetic Models of HPFs)*
- **University of Central Florida** *(Shock Tube Measurements of Intermediate Species and Flame Speeds of HPFs)*
- **Texas A&M University** *(Shock Tube Measurements of Intermediate Species and Ignition Delays of HPFs)*
- **King Abdullah University of Science and Technology** *(Mechanism Development. Shock Tube, Rapid Compression Machine (RCM), and Jet Stirred Reactor Experiments on Fuels for Kinetic Model Validation)*
- **National University of Ireland-Galway** *(Development of Base Mechanism. Shock Tube and RCM Experiments on Fuels for Kinetic Model Validation)*

Other collaborators:

Advanced Engine Combustion working group *(Semi-Annual Project Reviews with Industry Memorandum of Understanding Partners)*

Coordination:

- Bi-weekly team meetings, quarterly face-to-face leadership planning meetings, and an annual all-hands meeting
- Monthly stakeholder updates including technical highlights and deep-dive presentations – more than 85 individuals at 46 organizations across industry and other non-DOE governmental agencies

Remaining Challenges and Barriers

- Lack of understanding of the chemical mechanisms of non-linear blending for octane number, both synergistic and antagonistic
  - Important for all combustion strategies using gasoline like fuels
  - Non-linear blending for cetane number may also be important
- Detailed understanding of autoignition mechanisms and kinetics under a range of conditions for LDSI, mixed mode, and ACI blendstocks
  - RON and MON may not be accurate metrics at highly boosted conditions or "beyond MON" conditions – basic chemistry of why this happens is key
- Poor fundamental understanding of phi sensitivity, a property that is important for controlling combustion phasing in kinetically-controlled compression-ignition modes
- Detailed kinetics do not accurately predict PM precursor formation mechanisms for many compounds, and approaches for predicting sooting tendency from molecular structure are not yet robust
- The effect of chemical composition on the evaporation process for gasoline-like fuels is not accounted for in current models, including effects of HOV, non-idealities such as azeotrope formation, and composition evolution over the evaporation process

Proposed Future Research

- Experimental and theoretical studies of antagonistic and synergistic blending for octane number, and possibly cetane number
- Continued development of detailed data on autoignition mechanisms for a range of molecular structures, coupled with simulations, over a broad range of reaction conditions
- Fundamental studies of phi-sensitivity as well as targeted development of a standard test and metric for phi-sensitivity
- Studies that expand our knowledge of PM precursor formation and ability to predict soot formation tendency
- Foundational research on fuel evaporation and mixing with air, and how this is impacted by fuel chemistries well beyond those in conventional petroleum fuels
- Any proposed future work is subject to change depending on funding levels.

Summary

- Chemical kinetic models have been developed to predict fuel properties (e.g. ignition delay, RON, OS) for blendstocks blended into gasoline base fuels
- Computed maps of ignition delays over wide temperature and pressure range for blendstocks and Co-Optima core fuels (P/T ignition delay maps)

  Impact: Prediction of fuel properties at engine conditions allows engine researchers to evaluate different advanced combustion strategies
- Highly accurate approach for predicting which compounds have RON or OS over a specified level was demonstrated

  Impact: Provides a method to estimate RON and OS using less than 0.1 mL of a compound – highly valuable for screening proposed new fuels
- Flow reactor studies reveal mechanistic details of autoignition and PM precursor formation reactions

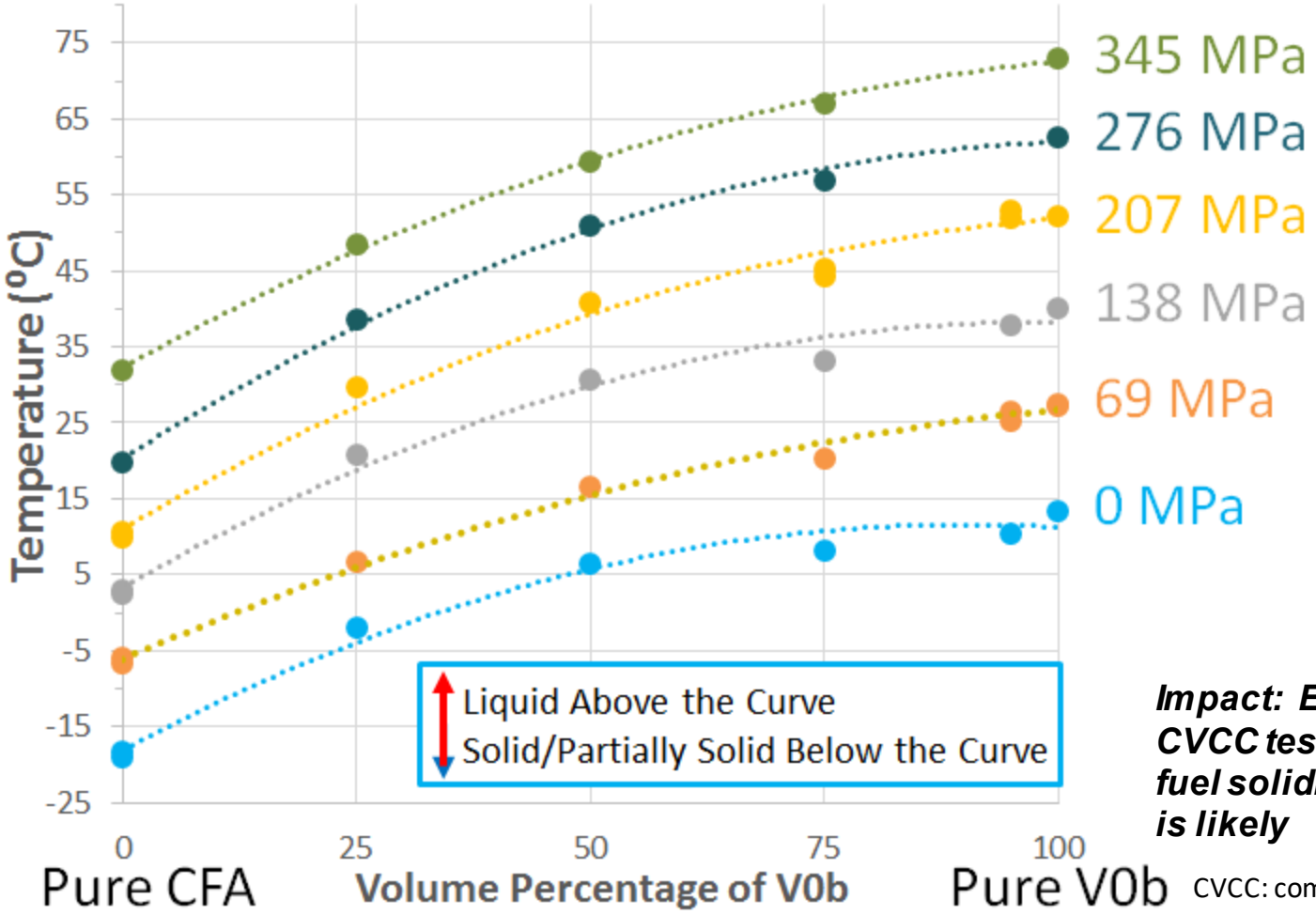
  Impact: An apparatus to reveal autoignition mechanisms and validate kinetic simulations has been developed and can be rapidly applied to a wide range of systems
- Research on composition/HOV evolution as fuel evaporates and the molecular basis for non-ideal behavior of alcohols reveals complex, non-ideal phenomena

  Impact: Fuel evaporation phenomena can impact autoignition, mixing, and pollutant formation

Technical Back-Up Slides

PNNL (Bays): High-Pressure Fuel Solidification
Accomplishment

Liquid-Solid Phase Change Diagram of Certification Diesel Fuel (CFA) in Diesel Surrogate (V0b)*



- Adding complex diesel fuel to Diesel Surrogate V0b was expected to significantly reduce the V0b final melting points (FMPs).
- FMPs were only slightly reduced for diesel concentrations up to ~50% at "low" pressures.
- Above 50% diesel, reductions in FMPs appeared to be more significantly reduced.
- At higher pressures, the effects of diesel addition were more greatly pronounced.
- Melting ranges increased
  - with increasing V0b
  - with increasing pressure

Impact: Enable engine, RCM, CVCC testing by identifying when fuel solidification or filter plugging is likely

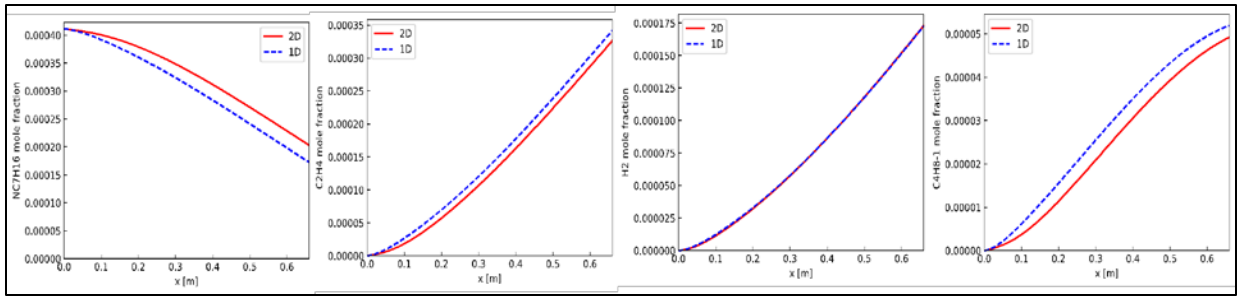
CVCC: compound vortex controlled combustion

*CFA and Diesel Surrogate work is being conducted in collaboration with the Coordinating Research Council, Project AVFL-18a. Diesel Surrogate V0b was developed under the auspices of AVFL-18a.

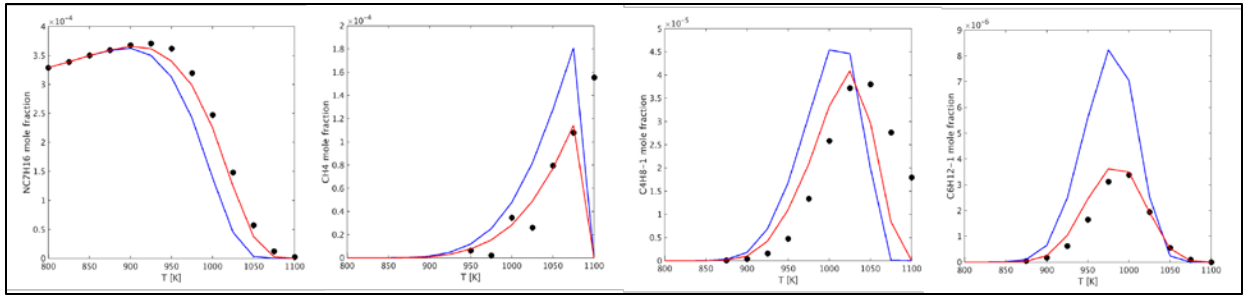
NREL (Fioroni/McCormick): Flow Reactor Autoignition Kinetic Mechanism Development and Validation *Accomplishment*

Flow reactor system dramatically upgraded to obtain higher quality data and focus on reaction mechanism studies

Modeling 1D versus 2D Effect



Validation of computational fluid dynamics model with n-Heptane



- Expanded capability through addition of dual gas chromatograph system for extensive analysis of combustion products
- System contains five detectors and five columns for speciation, identification, and quantitation of the full range of hydrocarbons as well as oxygenates and permanent gases

- 2D axisymmetric simulation is done for T = 1,000 K and τ_{res}=0.35s with reduced 88sp n-Heptane mechanism: 1D plug flow simulation with the same conditions is compared with the centerline results of 2D model – reactor functions as a plug flow reactor
- 1D plug flow simulation of heptane oxidation is performed using two different chemical kinetic mechanisms and compared with the flow reactor data. Co-Optima mechanism (red line), LLNL n-Heptane V3 mechanism (blue line). Agreement with Co-Optima mechanism is good